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ORNL-5049

**Coal Technology Program
Quarterly Progress Report No. 2
for the Period Ending March 31, 1975**

MASTER

OAK RIDGE NATIONAL LABORATORY

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COAL TECHNOLOGY PROGRAM
QUARTERLY PROGRESS REPORT NO. 2,
~~FOR THE PERIOD ENDING MARCH 31, 1975~~

AUGUST 1975

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
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for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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COAL TECHNOLOGY PROGRAM QUARTERLY PROGRESS REPORT NO. 2
FOR THE PERIOD ENDING MARCH 31, 1975

ABSTRACT

This report — the second of a series — is a compendium of quarterly progress reports for Oak Ridge National Laboratory research and development projects that are carried out in support of the increased utilization of coal as a source of clean energy. The progress reported for this period is for projects supported by the Division of Coal Conversion and Utilization and the Division of Advanced Research and Supporting Technology of the Energy Research and Development Administration, the Department of Housing and Urban Development, and the National Science Foundation.

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1. SUMMARY

J. P. Nichols

Highlights of progress through March 31, 1975, are summarized below:

° In hydrocarbonization research, the review and evaluation of existing process technology was completed. Significant contributions to the design of the 10-lb/hr pressurized bench-scale system for the hydrocarbonization of coal were made from ambient mock-ups including fluidization, recirculation, cyclone performance, solids feeding, solids transport, and solids withdrawal. The design is now complete and fabrication is underway. Also, operational testing of the high-temperature fluidized bed reactor has begun.

° Tests were initiated in the solid-liquid separations effort to examine the agglomerating tendencies of Char Oil Energy Development (COED) unfiltered raw oil (UFO) in the presence of various solvents. Examination of the insoluble portion by oil immersion microscopy showed that single-ring aromatic solvents produced significant agglomeration. Construction was begun on a 1-liter mixing-settling-filtration apparatus capable of handling high temperatures and high pressures. Coordinated analyses to determine the effect of aging on a solvent refined coal (SRC) sample were initiated.

° During this period the in situ gasification program completed the fabrication of a large block coal pyrolysis reactor. During preliminary testing, modifications to the tar trapping system, positioning of temperature probes, and air injection system were made. The first test of the unit employed western subbituminous coal.

° In chemical research and development, development of heterogeneous catalysts continues for desulfurization of coals. During the previous period a pulsed microreactor was designed and built. The reactor has been operated and applied to initial studies of the hydrogenolysis of thiophene and several thiophene derivatives and is designed to operate at gauge pressures of up to several atmospheres, with mixtures of H_2S-H_2 and with deuterium. An interesting finding during the period is not only that a mixture of H_2S-H_2 can be used to convert the catalyst to sulfide form, but that measurement of H_2S-H_2 ratio after a conversion appears to have a constancy characteristic of equilibrium relations. Work on the mini-autoclave system for studies of homogeneous catalysis has been stopped to accelerate the fabrication of the dynamic reactor system. In the physical structure of coals program, the results of a study on pyrite analyses have been completed.

° The work in analytical chemistry continues to develop and adapt analytical procedures and methods such as liquid and gas chromatography to molecular and trace element compositions of samples from coal conversion experimentation. In the preparative separations of coal-derived liquids studies, a modified Bureau of Mines--American Petroleum Institute procedure for the fractionation of heavy ends of petroleum has been used to separate four coal-derived liquids -- a medium oil from the COED process, a heavy oil from the Synthoil process, and two medium oils from the H-Coal process. In the liquid chromatographic studies, a series of solid absorbents have been evaluated for their ability to separate a COED medium oil.

° In an effort to estimate the costs of alternative levels or qualities of reclamation typical of Appalachia, in the systems studies of coal production, engineering and cost analyses of 28 model mines have been chosen for study because they represent various mining and reclamation techniques. Also, models are being developed for a process analysis estimation of cost functions for coal mining in the United States.

° Our quarterly progress in the Coal-Fueled MIUS project is being published separately. The work included continued conceptual design studies of the fluidized bed and heat exchangers as well as the initiation of fabrication of several models that will be used for cold flow testing of the fluidized-bed concept.

2. HYDROCARBONIZATION RESEARCH

H. D. Cochran, Jr.

This project for supporting research and development on coal hydrocarbonization is sponsored by the Division of Coal Conversion and Utilization of ERDA. Hydrocarbonization is an important type of coal liquefaction process that combines low temperature, high pressure, and fluidized-bed operation using hydrogen rich gas for fluidization. The hydrocarbonization process can produce desulfurized char, liquid fuels, and substitute natural gas. The relative yields of these products can be controlled. The char is suitable for use without stack gas treatment in fluidized-bed or traveling grate boilers. The liquid fuels include naphtha, light gas oils, and heavy gas oils. Conditions for hydrocarbonization include temperatures up to 1500°F (815°C) and pressures up to 150 atm (2200 psi).

Objectives and Scope of Work

The three objectives of the project are as follows:

- (1) Estimate the optimum conditions for operation of a fluidized-bed hydrocarbonization reactor.
- (2) Operate a fluidized-bed reactor capable of continuously processing 10 lb of coal per hour at temperatures up to 1200°F but at low pressure.
- (3) Conduct sufficient hydrocarbonization experiments to indicate that further work will be productive.

The scope of the project is limited as follows:

- (1) This project is restricted to the operation of a bench-scale hydrocarbonization reactor.
- (2) Background studies, analyses, and laboratory experimentation will be limited to that required to estimate the optimum conditions for operation of a hydrocarbonization reactor, to design this reactor, and to solve problems that occur during operation.
- (3) Experimentation will be conducted only with nonagglomerating coal and without catalysts.

Summary of Progress to Date

The milestone chart for this project is presented as Fig. 2-1. The review and evaluation of existing process technology (Task 1) was completed on schedule (Milestone 1) and a summary report was submitted to ERDA for review and should be released shortly.

The experimental development work (Task 2) has made important contributions to the design of the bench-scale system. Studies with ambient mock-ups including fluidization, recirculation, cyclone performance, solids feeding, solids transport, and solids withdrawal (Milestones 2 and 3) have supported the design of components for inclusion in the pressurized system. Assembly and operation of the high-temperature fluidized bed reactor (Milestones 4 and 5) were achieved during this reporting period. Initial operations of the high-temperature reactor have been of great value in demonstrating satisfactory performance in various aspects of this project while pointing out deficiencies and the need for further effort in others.

Task No. 3, which encompasses the design, construction, and operation of a pressurized bench-scale hydrocarbonization system, began during this reporting period. Design of the pressurized system was completed on schedule (Milestone 6) and craft work has begun. The prospects for beginning shakedown testing of the system on schedule (Milestone 9) have decreased somewhat as competing demands for craft work have increased significantly.

2.1 Review and Evaluation of Hydrocarbonization Data

J. M. Holmes, H. D. Cochran, Jr., M. S. Edwards,
D. S. Joy, and P. M. Lantz

Literature from eight carbonization and hydrocarbonization processes was reviewed; characteristics of these eight processes are summarized in Table 2-1. Since the information available for review was taken from the open literature, the process performances reported are those claimed by the developer of each process. Of the eight processes reviewed, only two — the Union Carbide hydrocarbonization process and the FMC COED process — have been developed through a significant engineering scale. Several of the processes that are based on relatively conventional technology have demonstrated moderate liquid yields [9.5 to 29.0% of the moisture- and ash-free (MAF) coal] which can be reasonably well correlated with process temperature and hydrogen partial pressure. The two processes producing the highest liquid yields — Schroeder and Garrett — depend on advanced technology and do not fit into the correlations based on temperature and hydrogen partial pressure. Apparently the effects of coal heat-up rate, product residence time, and/or local fluid dynamic conditions in the reactors have a very important, although poorly understood, effect on liquid yields. Estimates of the heat available from combustion of carbonization and hydrocarbonization reactor products

Milestones

1 Complete review and evaluation.	6 Complete design.
2 Begin fluidization and recirculation studies.	7 Obtain necessary approvals for operation.
3 Begin coal feeding and solids withdrawal studies.	8 Complete fabrication and installation.
4 Begin assembly.	9 Begin shakedown testing.
5 Begin high temperature operation.	10 Begin operation and experimentation.

Fig. 2-1. ORNL coal hydrocarbonization project milestone chart.

Table 2-1. Summary of carbonization and hydrocarbonization processes

Process	Union Carbide	U.S. Steel	Garrett	COED	C.S.I.R.O.	Schroeder ^a	USEM	Consol Fluidized Bed
Coal	Lake de Smet	Illinois No. 6	Western Kentucky	Illinois No. 6	Wallarrah, Australia	b	Hanna, Wyoming	Pitt Seam
Temp., °C	566	449-760	579	288-816	460	500	510	496
Pressure, psi	~1000	80-150	Approx. atmospheric	6-10	300-600	2000	Approx. atmospheric	10
Holdup time	5-11 min	~50 min	<2 sec	1-4 hr	37 min	<2 min	12 min	45-120 min
Yield, ^c %								
Char	38.4	66.4	56.7	60.7	83.0	b	60.9	b
Liquid	29.0	13.9	35.0	20.1	9.5	55.0	22.1	26.0
Water	19.2	5.1	1.7	5.7	5.5	b	6.5	b
Gas	16.2	14.6	6.6	15.1	3.0	37.3	7.3	b
Status of process development	15-ton/day pilot plant has been operated successfully on noncaking coals.	A 0.25- to 0.5-ton/day PDU under development; 100-ton/day pilot plant under design.	Results based upon 1-in.-diam reactor. Process to be tested in an available 3.6-ton/day pilot plant.	36-ton/day pilot plant has been operated	0.5-ton/day pilot plant has been operated.	Results from laboratory-scale experiments.	5-ton/day pilot plant has been operated.	1.5-ton/day pilot plant has been operated.
----- Estimate of reactor product available heat distribution (percentage of total heat from combustion of products)								
Char	42.8	60.2	50.4	63.5	83.8		65.2	
Liquid	36.9	15.9	41.6	28.8	12.7		30.3	
Gas	20.3	23.9	8.0	7.7	3.5		4.5	
Liquid-gas	57.2	39.8	49.6	36.5	16.2		34.8	

^aMolybdenum catalyst used.^bNot available.^cYields are presumably based on moisture- and ash-free coal, but for several references this could not be verified.
Yields are reproduced as published and are not normalized.

showed wide variations in product yield and, thus, in the distribution of the available heat among the char, liquid, and gaseous products. The Union Carbide and Garrett liquid products represent higher percentages (36.9 and 41.6 respectively) of the total product available heat than the other processes, while the Union Carbide and the U.S. Steel processes produce more available heat in the gases than the other processes.

Results of empirical regression of hydrocarbonization yield data indicate that very little reaction takes place below 400°C ; however, the yield of both oils and gases increases as the temperature is increased. A maximum oil yield is obtained between 550 and 600°C as shown in Fig. 2-2. Unlike the oil yield, Fig. 2-3 indicates the yield of hydrocarbon gases does not exhibit a maximum, but increases monotonically with temperature. At very high temperatures (1200°C), hydrocarbon gases are the principal product and only a few percent of the oils are recovered. Hence, the optimum temperature for the production of oils would be between 500 and 600°C .

Both the oil and gas yields increase with the partial pressure of hydrogen. This trend appears to continue up to 6000 psig; since essentially no data exist for higher pressures, it is not possible to determine whether this trend continues. The oil yield is apparently a function of the square root of pressure, and further increases above 6000 psig probably will not increase the oil yields substantially. Char yields decrease with increasing hydrogen partial pressure and increasing temperature as shown in Fig. 2-4.

Major problems with agglomeration in the hydrocarbonizer-fluidized bed probably will be encountered when strongly caking coals (bituminous) are fed to the system. However, there is some evidence that even weakly caking coals will tend to agglomerate if heated at a rate of $75^{\circ}\text{C}/\text{min}$ in a fluidized bed operating above 500°C . Methods that have been investigated for the prevention of agglomeration during carbonization include: (1) bed-recirculation procedures, (2) feed preoxidation, (3) feed heat treatment, (4) feed dilution procedures, and (5) stirred-bed operation. Of these methods, a bed-recirculation system¹ illustrated in Fig. 2-5 appears to be the most promising, and is probably the most practical solution. There is evidence that rapid recirculation of the bed and introduction of the fresh coal feed into the recirculating bed at high velocities will prevent the coal particles from sticking to each other long enough for the coal to be devolatilized; it will thus become nonagglomerating.

A lock-hopper system coupled with either rotary valves or a star feeder is recommended for feeding coal solids to the hydrocarbonizer reactor. Slurry feeding was considered for this system, but it was rejected because of pump erosion and heat balance considerations.

Preliminary calculations concerning process thermal efficiency indicate that the maximum superficial bed velocities should be limited to about 3 fps for a 300 -psia operating pressure, and 0.5 fps for a

ORNL DWG 75-1096R1

Fig. 2-2. Oil yields as a function of temperature in a fluidized bed hydrocarbonization reactor.

ORNL DWG 75-1097

Fig. 2-3. Total gases produced in a fluidized bed hydrocarbonization reactor.

ORNL DWG 75-1099

Fig. 2-4. Amount of char produced in a fluidized bed hydrocarbonization reactor.

Fig. 2-5. Recirculation bed concept. [Reproduced from Vol. 1, EPA 650/2-73-048c (December 1973)]

2000-psia operating pressure, thus maintaining the weight ratio of recycle gas to coal-feed below 5/1. This limit may be exceeded if complete recovery of the heat from the reactor-product gases can be achieved. The problems of product recovery and heat recovery from the reactor effluent gases are interrelated. The heavy tars tend to foul conventional heat exchanger surface. If a wash is used to prevent tar deposition in the heat exchanger, it will be necessary to use as high a wash temperature as possible to avoid gross heat inefficiencies.

Desulfurization of the oils and tars produced by hydrocarbonization will be mandatory if these products are to be used as fuels for boiler consumption. Hydrotreating should remove 95% of the sulfur, and should produce syncrudes that are suitable for gasoline blending and the production of No. 4 fuel oil. Desulfurization of the chars produced by hydrocarbonization may be achieved by a combination of coal-feed beneficiation and removal of H_2S from the gases recycled to the hydrocarbonizer. However, if the char is to be used only for the production of hydrogen and process heating requirements, beneficiation will not be necessary, since the sulfur remaining in the char can be removed subsequent to gasification of the char.

2.2 Experimental Development

R. E. Barker and F. J. Endelman

Work Accomplished

Ambient Mock-Ups. - Several ambient temperature and pressure experiments have been conducted to support design of the bench-scale system. A 4-in.-diam Lucite fluid bed (Fig. 2-6) has been used to obtain pressure drop and minimum fluidizing velocity data for coal particles. Figure 2-7 is an example of the data obtained using the mock-up. The results of the experiments are in good agreement with correlations published in the open literature.

Operation of a coal feeding device has been shown to meter an easily controllable coal feed rate to a fluidized system. The feeder consists of a ball valve with the stem modified so the valve can be continuously rotated and the bore of the ball blocked to form two cups in the ball and to close the ball to continuous flow. When the valve is rotated one revolution, two cupfuls of coal are delivered from the hopper to the system below the ball valve. For testing purposes a 1/2-in. Whitey ball valve was modified, connected to a hopper, and allowed to discharge into a container supported by a load cell. The valve was driven by a variable-speed motor and the weights measured by the load cell were recorded on a strip-chart recorder. The strip chart record was graphically differentiated to obtain the coal feed rate. Figure 2-8 is a plot of the coal feed rate vs the shaft speed. The graph shows that coal feed rate is a linear function of the shaft speed. The slope of the line represents the amount of coal fed per revolution, 2.35 g, independent of shaft speed. The strip chart record for each run was linear showing that the coal feed rate was steady.

Fig. 2-6. Flowsheet for fluidization studies.

Fig. 2-7. Pressure drop vs velocity.

ORNL DWG. 75-687

Fig. 2-8. Modified ball valve feeder data.

After about 6 hr of operation, the ball valve feeder was disassembled for inspection. Although some coal had deposited on the Teflon seats, there was no evidence of permanent damage. After lengthy operation, it is likely that the seats would be damaged, but operability for at least the duration of one run appears to be feasible.

High-Temperature Studies. - Design, fabrication, installation, and first operation of the atmospheric pressure hydrocarbonization system was achieved. For our first experiment, Run No. AHC-1, 4 lb of subbituminous coal from the Wyodak seam of Campbell County, Wyoming, were charged to the 4-in.-diam reactor. At a bulk density of 37 lb/ft³, the bed height should have been 12 in. Nitrogen was fed to the reactor through the preheater at a constant rate of 0.28 scfm.

To expedite the installation and possible subsequent modification of the preheater after this shakedown run, no packing was used for this experiment. Even so, an outlet gas temperature of 800°F was obtained after 4 hr of heating. The clam shell furnaces on the reactor itself did an excellent job of supplemental heating. A fluid bed temperature of 1000°F was attained after 2-3/4 hr, and was manually controlled for two additional hours before power shutdown. Throughout the course of the experiment, continuous bed pressure drop measurements revealed no instabilities in fluidization.

Numerous gas, liquid, and solid samples were obtained for chemical analysis during Run AHC-1. These were reported in detail in the monthly progress report for March. All mechanical aspects of the design performed very well. No abnormal temperatures or pressures were observed during the 6-hr experiment although several instrument and electrical malfunctions did occur. All of these were corrected without difficulty after the experiment.

A second carbonization experiment, Run AHC-2, was attempted during the quarter. Its objectives were to examine the reproducibility of results obtained in Run AHC-1 and to further shake down our equipment. After 80 min of operation, a large leak was observed in the flanged connection on top of the reactor. The equipment was immediately shut down. Subsequent examination of the connection revealed a complete gasket failure, apparently resulting from uneven compression.

Several design changes were made during the quarter. To prevent the loss of heat and the condensation of high boiling material on the piping interior, heating elements, heat transfer cement, and insulation were mounted externally on all intervessel piping, tees, and reducers. A tripod-like sheath was slipped onto each interior 1/8-in. thermocouple to keep the tip from contacting hot vessel walls. In addition, all thermocouples in the reactor, preheater, and condenser inlet were rearranged to enter each vessel through a blind flange on a tee at the top or bottom of the vessel and then to run axially within the vessel. A short section of 1-in. pipe was welded into the side of the reactor top reducer and preheater top tee to facilitate loading.

To decrease the amount of scrubber water accumulated during each experiment, the batch condenser was converted to a recirculating system. A small centrifugal pump now withdraws water at a point 9 in. from the bottom of the barrel, and sends it back through the inlet spray nozzle via a rotameter and heater exchanger. The former second stage barrel of the condenser is retained as an overflow holding tank.

Work Forecast

Ambient Mock-Ups. - Work with the ambient mock-ups will be continued, with relatively low priority, as time permits. Further studies will be made on recirculating fluidized bed performance using different draft tube geometries. The effect of gas viscosity will also be studied briefly. Evaluation of a solids flow meter, utilizing heat transfer as an indicator of solids flow, will be performed using the calibrated solids feeder. Finally, integrated operation of the feeder, pneumatic solids transport, recirculating fluidized-bed operation, and solids withdrawal will be demonstrated using the mock-ups on hand.

High-Temperature Studies. - At least one run will be conducted each month of the next quarter. Our goal is to achieve a maximum normal turnaround time of 2 weeks. The installation of safety related instrumentation, a prerequisite for operation with H_2 , will also take place in the next quarter. It is expected that this equipment can be completed in time to have a hydrogen run within the quarter. Several additional design changes also will be made in the quarter. These include replacement of the reactor furnaces with surface mounted electrical heaters, addition of thermal radiation shielding to interior thermocouples, fabrication of a sampling cylinder manifold for better evacuation and sealing, addition of a cyclone external to the reactor, and addition of an exhaust gas flow meter for closing the material balance.

2.3 Bench-Scale Studies

H. D. Cochran, Jr., J. M. Holmes, and T. W. Pickel

Work Accomplished

Design and Analysis. - Conceptual design of the pressurized portion of the bench-scale hydrocarbonization system (Fig. 2-9) included the following design objectives: (1) coal feed rate, ~ 10 lb/hr, (2) pressure vessel design for 350 psig and 1250°F (higher pressures will be attainable at lower temperatures), (3) gas superficial velocity in the reactor, ≤ 2 ft/sec. The flowsheet includes a coal feed hopper with a mechanical feeder, a gas preheater, a hydrocarbonizer, a char receiver, a water scrubber, a dry-ice temperature cold trap, and a filter. Each of these components is discussed below.

Fig. 2-9. Bench-scale hydrocarbonizer.

The coal feed hopper is designed to operate at the system pressure (≤ 350 psig) and at a temperature up to 600°F . This ample temperature allowance will permit use of the feed hopper in a batch mode as a coal drier and/or preoxidizer in preparation for a hydrocarbonization run.

The gas preheater is designed to heat the feed gas stream (~ 66 scfm) to $\sim 1250^{\circ}\text{F}$.

The hydrocarbonization reactor is constructed from a 3-ft section of 4-in. NPS, sched 80, type 316 stainless steel pipe with an expanded 6-in. NPS, sched 80 section above for disengagement. Provision is made for feeding coal either to the side of the reactor or to the bottom. Three alternate char overflow lines are provided at 3, 5, and 7 diameters above the gas distributor. The reactor is flanged top and bottom and contains an internal cyclone in the upper expanded section.

The char receiver is of similar design to the feed hopper except that sched 80 pipe and a 600-lb flange are used to allow operation at higher temperatures.

The water scrubber is designed to "knock out" the bulk of coal liquids including aerosols. Construction of sched 80, type 316 stainless steel pipe will allow operation at higher temperatures if, for example, testing of an organic scrub is desired.

The dry-ice temperature cold trap is intended to condense lighter organic liquids before the process gas stream is filtered and vented. Water vapor from the scrubber will also be condensed. If water vapor carryover from the scrubber places too heavy a load on the dry ice temperature cold trap, an ice water temperature cold trap will be installed ahead of the dry ice temperature trap with condensed water recycled to the scrubber.

Design of a hydrogen supply station with space for two hydrogen tube trailers has been completed. Design of necessary changes to existing facilities in Building 2528 including ventilation and isolation of the process area has also been completed. Work has been started on a formal safety analysis report for the bench-scale system. This report, required by laboratory management, will address the explosive hazards of the hydrogen and hydrocarbon gases as well as the toxic hazards associated with the polycyclic aromatic hydrocarbons present in coal liquids.

Fabrication and Installation. - Work has begun on the necessary modifications to facilities in Building 2528. Work accomplished to date includes thorough cleaning and decontamination, repairs to door latches, locks, etc., removal of the ceiling in the process area to eliminate a hazardous stagnant air volume and to provide additional head room, and removal of some old ventilation duct work and electrical conduits.

Work Forecast

Design and Analysis. - Completion of the safety analysis and the safety reviews and approvals are expected during the next quarter. The only remaining effort in this category will involve flowsheet analysis and interpretation of experimental results once the experiment is operational. In preparation for this need, shakedown runs with a purchased process analysis computer program (Phillips Petroleum Company's PDA Code, marketed by McDonnell-Douglas Automation Company) will be initiated.

Fabrication and Installation. - Pressure vessels for the bench-scale system will be fabricated in the Laboratory's shops. Modifications to Building 2528 will be completed. Installation of the system for shakedown testing will follow immediately. Although there is still some chance of completing installation during the next quarter, some slippage appears likely.

Operation. - Shakedown testing of the bench-scale system is scheduled to start near the end of the next quarter. It appears that some slippage in the completion of installation may postpone the start of shakedown testing until the following quarter.

2.4 References

1. W-C. Yang and D. L. Keairns, "Recirculating Fluidized Bed Reactor Data Utilizing a Two-Dimensional Cold Model," presented at the 75th National Meeting, AIChE, Detroit, Mich., June 3-6, 1973.

3. SUPPORTING RESEARCH AND DEVELOPMENT IN SEPARATIONS TECHNOLOGY

B. R. Rodgers

This project for supporting research and development on separations technology for coal conversion systems is sponsored by the Division of Advanced Research and Supporting Technology of ERDA and is authorized by Work Order No. 3 under Contract No. 14-32-0001-1740.

The work in the first year will focus on alternative methods for accomplishing the solid-liquid separations that are required for liquefaction processes. The first phase, completed January 18, 1975, consisted of the review and evaluation of available data. Phase II will consist of characterization tests of selected process streams and scouting tests for some alternative separations methods. A third phase will initiate bench-scale development of one or more types of promising methods.

Summary of Progress this Quarter

Tests were initiated to examine the agglomerating tendencies of Char Oil Energy Development (COED) unfiltered raw oil (UFO) in the presence of various solvents. Examination of the insoluble portion by oil immersion microscopy showed that single-ring aromatic solvents produced significant agglomeration. Further separations, using both sedimentation and centrifugation, determined the amount of agglomerated or insoluble material present in the solvent-UFO mixtures. The solvents were ranked according to their ability to dissolve UFO. Finally, filtrations through sub-micron membranes were used to compare the filterability of the mixtures. The filterability tests are not complete, but differences were demonstrated.

Particle size analyses on H-Coal solids by electron microscopy showed that 50% by volume of the particles were $< 1 \mu$ in diameter. Optical and coulter counter techniques were not applicable due to the small particle size.

Characterization analyses on the COED filtered and unfiltered oil showed nearly all the solids were removed by the process filtration cycle, leaving a lighter, less dense material with more volatile matter and one-third less fixed carbon. The solids contained nearly all the ash and a significant amount of highly unsaturated organic material.

Construction was begun on a 1-liter mixing-settling-filtration apparatus capable of handling high temperatures and high pressures. Coordinated analyses to determine the effect of aging on a solvent refined coal (SRC) sample were initiated.

3.1 Review and Evaluation: Phase I Report

B. R. Rodgers and M. S. Edwards

The Phase I review and evaluation were completed. A thorough review of the literature and current process technology was made with special emphasis on the study of past and present methods for separating micron-sized solids from the viscous streams that result from the hydroliquefaction and pyrolysis of coal. The separations methods being used or under study in the major processes (SRC, COED, H-Coal, and Synthoil) were examined by site visits and discussions with principal investigators.

An oral presentation of Phase I results and experimental plans for Phase II was given at the Office of Coal Research on January 13, 1975. The final Phase I report was prepared and issued as ORNL-TM-4801.

3.2 Characterization Tests of COED Filtered and Unfiltered Oil from Western Kentucky Coal

B. R. Rodgers

Table 3-1 gives the analytical results of initial characterization tests on unfiltered raw oil (UFO) and filtered oil (FO) from the COED process.

Interesting observations to be made from the comparisons of unfiltered oil with filtered oil are:

- (1) The carbon/hydrogen ratio decreased, indicating that highly unsaturated hydrocarbons were removed with the solids.
- (2) Nearly all of the ash (inorganics) was removed by filtration.
- (3) The contents of the following elements were significantly reduced: aluminum, boron, calcium, chlorine, potassium, manganese, sodium, and nickel.
- (4) The contents of the following elements were significantly increased: iron, magnesium, silicon, strontium, and vanadium.

The increase in magnesium and silicon could be due to carrythrough of the precoat material. The strontium and vanadium results are not consistent when unfiltered oil is compared with filtered oil and filter cake holdup. The large increase in iron content is not understood since most pyritic compounds are removed with the solids. Possibly the latter value reflects material from the process vessels.

Table 3-2 gives additional analyses on COED unfiltered and filtered oil. These data show that nearly all the solids were removed, leaving a

Table 3-1. Characterization Analyses of COED Process Materials

	Unfiltered Raw Oil	Filter Cake	Filtered Oil	Change (FO-UFO)
Carbon	81.0		82.9	+1.9
Hydrogen	7.18		7.77	+0.59
Nitrogen	1.20		1.23	+0.03
% Ash	2.05		0.04	-2.01
Molecular weight	266		289	+23
<u>Trace Elements^a (ppm)</u>				
Al	5,000	10,000	2,000	-3,000
As	3	7	2	- 1
B	200	200	100	- 100
Ba	1	10	1	0
Bi	< 0.3	<0.3	<0.3	0
Br	0.7	<0.2	0.1	- 0.6
Ca	3,000	3,000	1,000	-2,000
Cd	< 0.3	< 0.3	< 0.3	0
Cl	100	20	20	- 80
Co	0.2	2	0.3	+ 0.1
Cr	2	2	2	0
Cs	1	0.5	0.6	- 0.4
Cu	2	10	2	0
F	2	10	2	0
Fe	7,000	10,000	15,000	+8,000
Ga	0.5	2	0.2	- 0.3
Ge	0.8	1	1.0	+ 0.2
K	250	500	200	- 50
La	1	5	2	- 1
Mg	200	500	500	+ 300
Mn	5	10	2	- 3
Mo	0.5	20	<0.5	?
Na	100	500	50	- 50
Nb	0.1	0.4	0.2	+ 0.1
Nd	2	5	3	+ 1
Ni	30	50	7	- 23
P	10	70	10	0
Pb	1	10	1	0
Pr	0.5	3	1	+ 0.5
Rb	0.5	2	0.3	- 0.2
Sb	< 0.2	0.1	< 0.2	0
Sc	1	1	1	0
Se	< 0.1	0.4	0.1	0
Si	7,000	15,000	15,000	+8,000
Sn	< 0.3	< 0.3	< 0.3	0
Sr	5	30	10	+ 5
Ta	< 1	< 1	< 1	0
Te	< 0.5	< 0.5	< 0.5	0
Th	0.2	0.6	0.2	0
Ti	50	100	50	0
Te	0.5	3	0.5	0
U	0.7	2	0.6	- 0.1
V	5	30	15	+ 10
W	< 0.5	2	< 0.5	0
Y	1	5	2	+ 1
Zn	3	10	4	+ 1
Zr	3	20	1	- 2

^aFrom Analytical Chemistry Division Research and Development Summary February 1, 1975. Trace analyses were by spark source mass spectrometry using an added internal standard. The data should be considered as semiquantitative as some results will vary by a factor of 2. The method has proven applicable and will be developed further.

lighter, less dense material with more volatile matter and one-third less fixed carbon. It is surprising that the sulfur values are as close before and after filtration. Generally one-third to one-half of the sulfur is associated with the inorganic (ash) portion. These data indicate that nearly all the sulfur was associated with organic material.

Table 3-2. Characterization analyses of COED oils from Western Kentucky coal

	Fixed carbon (%)	Volatile matter (%)	Organic sulfur (%)	Inorganic sulfur (%)	Total S (inorg. and org.)	Density (g/cc)	Total solids ^a
UFO ^b	15.6	82.4	1.46	0.032	1.49	1.145	8.16
FO ^c	10.1	89.9	1.43	<0.0001	1.43	1.109	0.03

^aReported as quinoline insolubles.

^bUFO = unfiltered oil.

^cFO = filtered oil.

3.3 Agglomeration of Solids: Optical Evaluations

B. R. Rodgers, P. R. Westmoreland, and D. A. McWhirter

The effect of solvents on the agglomerating tendencies of solids in the UFO from the COED process was examined by oil immersion spectroscopy. Particular attention was given to the agglomerating tendencies of the solids in the presence of the solvents. Also, a number of potential separation techniques were observed. These are discussed below.

In all cases, slides were prepared by spreading a thin film of UFO onto a slide glass with the aid of a razor blade. A drop of solvent was then deposited in the center of the UFO film, and a cover glass was placed over the area of the drop. Most observations were made at 970X using oil immersion techniques. Figure 3-1 shows the UFO film only, and serves as a base line for comparison of other slides.

Fig. 3-1. Unfiltered raw oil from the COED process.
Magnification, 1000X.

The Agglomerating Effect of Toluene

Figures 3-2 and 3-3 show the latter stages of an agglomeration produced by toluene. Unlike the UFO slide, nearly all particles are associated and the area between agglomerates is relatively clear. In the initial stages of agglomeration, small "bridges" of submicron particles covered with an oil solution lined up to facilitate the transfer of liquid and particles from one agglomerate to another.

The Interfacial Effect of Tetrahydrofuran

Figure 3-4 shows that, in the two-phase system UFO-THF, particles tend to collect at the interface. There was a definite separation of particles into three categories: those that remained in the "oil-rich" phase, those that remained in the "THF-rich" phase, and those that collected at the interface. Some particles could be seen to bombard the interface from the oil-rich side, penetrate a short distance, and then be repelled rapidly. Others would penetrate the THF-rich phase and remain there, while another significant portion collected at the interface between the two phases.

The Flotation Effect of Quinoline

During the initial dissolution produced by quinoline, many small particles tended to agglomerate and float to the top of the film. The larger particles remained near the bottom and were well dispersed. After sitting for several days, most of the small particles were still found at the top but were not nearly as agglomerated. The initial agglomeration seemed to be encouraged by an oil-rich phase which was held within the agglomerate. Apparently this oil-rich phase was eventually dissolved by the quinoline and the agglomerates were separated.

Separations Schemes Indicated by These Studies

These studies indicate effects that were not found in the literature search performed previously.¹ They indicate the possibility of solids separation by three mechanisms: agglomeration (toluene), interfacial concentration (THF), and flotation (quinoline). However, optical evaluations of well mixed and aged slurries showed that the latter two effects occur only during initial dissolution. The agglomerating effect of toluene was still present in the well mixed dispersions. Agglomeration was also produced by other aromatic solvents such as benzene and xylene.

3.4 Solvent Extraction of COED Unfiltered Oil (UFO)

B. R. Rodgers, P. R. Westmoreland, and D. A. McWhirter

Sedimentation and Centrifugation

The large agglomerates in the toluene-UFO mixtures suggested that solvent extraction followed by settling or centrifugation might be a viable separation scheme. To examine this possibility, COED-UFO

Fig. 3-2. Unfiltered raw oil (COED) with toluene added.
Scene 1: magnification, 1000X.

Fig. 3-3. Unfiltered raw oil (COED) with toluene added.
Scene 2: magnification, 1000X.

Fig. 3-4. Unfiltered raw oil (COED) with tetrahydrofuran added. Magnification, 1000X.

was extracted at room temperature with the solvents listed in Table 3-3. First, 12 parts solvent was poured into 1 part UFO and mechanically stirred for 10 min, after which the mixture was poured into four 15-cc centrifuge tubes or into a 35-cm settling column. The centrifugations were at 3800 rpm and the quantity of heavy phase was determined by identifying the interface with a point light source and reading the calibrated marks on the centrifuge tube.

The settling rates, shown in Fig. 3-5, are preliminary but show promise for such a process. However, the economics would depend to a large extent on the solvent recovery step and the degree to which the inorganic sulfur accumulated in the heavy phase. Electron microscope photon emission spectroscopy indicated that most of the pyritic sulfur was in the heavy phase.

Centrifugation after fractionation also produced an effective separation. Slides of the light phase showed that there were very few particles remaining. At the top of the 50-cm column, the light phase particles were approximately 3 to 5 μ in diameter; the heavy phase contained individual particles up to 30 μ but mostly in an agglomerated state. Benzene and xylene insolubles were agglomerated similar to toluene.

The results of centrifuging the extraction mixtures are shown in Table 3-3. These data indicate that aromatics containing a nitrogen atom in the ring structure (quinoline, pyridine) are excellent solvents, as are polar molecules containing oxygen (tetrahydrofuran, acetone). The amount of material extracted by all solvents was sufficient to qualify them as potential candidates for a solvent extraction process. The important parameters (other than economics) that remain to be determined are the mineral split (particularly sulfur) between the two phases, solvent holdup in the heavy phase, and the ease of solvent recovery. Currently the effect of the above solvents on filtration rates is under investigation.

Table 3-3. Solvent extraction of COED unfiltered oil (UFO) from Western Kentucky coal

Solvent	Solvency rank	(cc heavy phase/g UFO)
Quinoline	1	0.1
Tetrahydrofuran	2	0.2
Pyridine	3	0.2
Acetone	4	0.2
Toluene	5	0.5
Xylene	6	0.8
Benzene	7	0.8

Fig. 3-5. Settling rate of toluene insolubles.

3.5 Particle Size Distribution of H-Coal Solids

B. R. Rodgers and M. H. Eager

Particle size distributions were determined on a sample of filtered solids from the H-Coal process. The solids had been obtained by Hydrocarbon Research, Inc. (HRI) by filtering a 50/50 mixture of vacuum still bottoms and Ashland APO oil through their bench-scale plate filter. The above mixture simulated the filtration stream in the actual H-Coal process, and particle size results should be comparable.

One of the main objectives in the initial particle size determinations was to evaluate available particle sizing techniques as they relate to colloidal particles from coal liquefaction streams. The H-Coal streams have proven to be among the most difficult to filter, and thus they provided a severe test. In this particular case the well dispersed particles were too small to be measured by either optical microscope or coulter counter. The electron microscope proved to be the only applicable instrument. Figure 3-6 illustrates the difficulty involved in filtering and measuring these particles. Shown is a photomicrograph of the H-Coal particles at 15,523X magnification. Even at this high magnification many of the particles are barely resolvable. Figure 3-7 gives a number and volume percent particle size distribution as determined from the electron micrograph and a Zeiss counter. The colloidal nature of these solids is demonstrated by the fact that one-half of the total number were less than 0.11μ and one-half of the total sample volume were less than 0.98μ .

It is not anticipated that unfiltered material from the COED and SRC processes will contain as many small particles as the above sample. Optical microscope results to date show a much broader particle size distribution for the COED material with a significant portion of the particles above 10μ .

If only optical techniques were used, it is obvious that considerable error might be involved in particle size determinations of materials similar to the H-Coal sample. As an indication of this error, the Zeiss counter was used to determine the particle size distribution of the 2000X photomicrograph shown in Fig. 3-8. The volume percent distribution was:

Diameter at 90%	8.59μ
Diameter at 50%	4.16μ
Diameter at 10%	0.86μ

These values compared to those in Fig. 3-7 show considerable error due to poor resolution of the very small particles.

ORNL DWG 75-862

15,532 X

Fig. 3-6. Particle size distribution of H-Coal particles.

Fig. 3-7. Particle size distribution of H-Coal particles.

ORNL DWG 75-861

2000 X

Fig. 3-8. Optical photomicrograph of H-Coal particles.

3.6 Identification of Pyritic Sulfur in COED Unfiltered Oil

B. R. Rodgers, L. A. Harris, and L. D. Hulett

It is important to know the particle size range that includes the sulfur containing minerals. Different methods of separation would be indicated depending on whether this material was present as occluded portions of large particles or small separate particles. It is also important to determine if the mineral matter is in the heavy phase of a solvent fractionation. A qualitative evaluation of the pyritic sulfur distribution using an optical microscope with polarized light indicated that most of the pyritic sulfur was associated with the smaller particles. Of course, the pyritic material could have been present as very small impurities within the larger particles, and consequently would not have reflected light.

The question of pyrite distribution was determined on a small number of samples by using a 30,000 eV electron microscope and measuring the resulting energy distribution of photon emissions. Since the photon emission energy is a characteristic parameter of a given element, iron and sulfur could be identified as occurring together in a given particle.

A number of particles were examined in both the light and heavy phase from a toluene fractionation of a COED unfiltered oil. There appeared to be no pyritic sulfur in the toluene soluble fraction although organic sulfur was identified. Pyritic sulfur was identified qualitatively in the heavy phase material.

3.7 Temperature-Viscosity Behavior of COED Unfiltered Oil

P. R. Westmoreland, B. R. Rodgers, and D. A. McWhirter

Viscosity of COED UFO was measured over a temperature range of 58 to 145°C (136 to 293°F). The oil was produced from a Western Kentucky coal, and had been stored in steel cans. A 1500-ml sample was analyzed with a Brookfield LVT viscometer, using various shear rates at each temperature. High and low temperatures were normally alternated.

Theoretically, viscosity η of a pure liquid is related to absolute temperature T by:

$$\log \eta = \frac{a}{T} + b .$$

Experimental data on the COED UFO (see Fig. 3-9) approximately agrees with this expression at temperatures less than about 100°C ($1/T > 2.7 \times 10^{-3}$). However, at higher temperatures the experimental relationship deviates sharply from theory. Such deviation is expected from the complex mixture of organic compounds and is also exhibited in other published COED viscosity data.²

Fig. 3-9. Temperature-viscosity behavior of COED unfiltered oil.

Non-Newtonian characteristics of the oil were investigated by varying shear rates at constant temperature. Table 3-4 gives examples of the variations found at various rotational speeds. For comparison with other oils and with COED filter oil, the variations were ignored. A logarithmic mean of data points was used to produce Fig. 3-9.

Table 3-4. Effects of shear rate on COED UFO viscosity

	Speed (rpm)	Viscosity (cp)
Spindle 3, 58°C	0.3	62,400
	0.6	60,000-70,600
	1.5	50,000-62,800
Spindle 1, 144°C	30	23.6-24.8
	60	25.3-26.6

3.8 Sample Coordination

B. R. Rodgers and A. G. Draeger (Catalytic Inc.)

To date samples have been received from COED, Synthoil, H-Coal, and Southern Services SRC. During a visit to the SRC plant at Wilsonville, Alabama, an agreement was made to coordinate physical property measurements made on the plant site with those made at varying intervals at ORNL. The above is intended to ascertain the effect of sample storage time and conditions on physical properties. Table 3-5 gives the materials and analyses to be made.

Table 3-5. Coordinated analyses of ORNL/Catalytic Inc.
on solvent refined coal streams

Analyses	Filter feed	Filtrate	Filter cake	Product coal	Solvent stream
Density	X	X			X
Ash, %	X	X	X	X	
Sulfur, %	X	X	X	X	X
Inorganic	X	X	X	X	X
Organic	X	X	X	X	X
Solids, %					
Filtration	X	X			
Cresol insolubles	X	X	X	X	
Solvent, %			X	X	
Viscosity @ 250°F	X	X			
Viscosity @ 500°F				X	
Ultimate analyses			X		
Proximate analyses				X	
Gel chromatography		X		X	X

3.9 Bench-Scale Mixer, Filter, and Settler

To facilitate the agglomeration/flocculation studies, a small-scale (1-liter) system has been designed and is being constructed (see Fig. 3-10). The 1-liter stirred autoclave will be used to evaluate various agglomerating agents and can be operated at high temperatures (to 700°F) and high pressures (to 1000 psia).

The filter is a simple, circular plate filter that can be used with metal discs of controlled porosity, filter papers, or precoats. The settling chamber is heated and will have sample ports every 6 in. to facilitate sampling for particle size analyses. Both vessels have high-temperature characteristics (700°F) and moderate pressure capabilities (500 psia). The apparatus is expected to be in operation within 2 months.

3.10 Work Forecast

Pretreatment and Solids Concentration

Solvent fractionations followed by centrifugation and millipore filtrations are planned for the SRC unfiltered product oil (UPO). Following this, 1-liter filtrations and/or sedimentation will be used to evaluate the most promising solvents for both SRC and COED processes. Hydroclones will be evaluated in conjunction with these batch operations.

Process Stream Characterization

- (1) Viscosity-temperature measurements at elevated temperatures and pressures will be made on COED and SRC materials with a new Norcross falling ring viscometer.
- (2) Elemental and proximate analyses will be made on the SRC process samples. The physical property measurements listed in Sect. 3.8 will ascertain the effect of aging and further characterize the samples.
- (3) The attempt to identify the particle size and shape of pyritic sulfur in process materials from COED and SRC will continue.

Fig. 3-10. Bench-scale mixer settler/filter.

Milestones

The projected completion dates for the work forecasted above are as follows:

- (1) Solvent fractionation/centrifugation/millipore filtrations of SRC UPO - June 1, 1975.
- (2) Bench-scale filtrations/sedimentation of selected solvent/oil mixtures - August 1, 1975.
- (3) Viscosity-temperature measurements of SRC and COED materials at elevated pressures - September 1, 1975.
- (4) Hydroclone evaluation - October 1, 1975.
- (5) Characterization of COED and SRC process streams - October 1, 1975.
(NOTE: These should continue into the next fiscal year.)
- (6) Recommendation and design of bench-scale process for further separation studies - October 1, 1975.

3.11 References

1. M. S. Edwards, B. R. Rodgers, and R. Salmon, Supporting Research and Development on Separations Technology: Phase I Report, ORNL-TM-4801 (March 1975).
2. Char-Oil-Energy Development, U.S. Dept. of the Interior, Office of Coal Research, OCR Report No. 73, Interim Report No. 2, prepared by the FMC Corporation (April 4, 1974).

4. EXPERIMENTAL ENGINEERING SUPPORT OF AN IN-SITU GASIFICATION PROCESS

R. C. Forrester III and P. R. Westmoreland

Installation of a large block pyrolysis reactor (Fig. 4-1) was completed in mid-January and preliminary tests of the apparatus were begun. An uninstrumented block of Appalachian coal (an eastern Kentucky bituminous) was used for the first test though later tests have been performed upon western subbituminous coals taken from the Roland-Smith seam. Figure 4-2 describes the heating rate observed during reaction, whereas the product gas composition on a nitrogen-free basis is shown as Fig. 4-3.

The first experiment was terminated before the maximum design temperature could be attained when the tar trapping system appeared to be performing inadequately. As a result, a small experiment is being constructed to perform quick scoping tests of various trapping techniques. Systems to be surveyed include electrostatic precipitation, impingement trapping, spray scrubbing, and sparging. These tests should be completed later this fiscal year.

Large block pyrolysis experiments were resumed following construction and installation of an improved tar trapping system. Pyrolysis fluid effluents presently flow to a 4-in.-ID disengagement vessel 3 ft in length where both vapors and the hydrocarbon liquid aerosol are removed. An internal cooling coil promotes condensation of water and light hydrocarbon liquids, whereas glass packing at the vessel exit is used to disengage the aerosol. Residual aerosol particles are subsequently removed by cartridge-type string filters.

Ten 55-gal drums of lump coal, taken from the Roland-Smith seam, have been received from Wyodak Resources, Inc., of Gillette, Wyoming. (Use of this particular coal was recommended by Jerome Dow of the Lawrence Livermore Laboratory during our visit there in January. Laboratory studies of in-situ processing at LLL also utilize Roland-Smith coal.) Several of the larger blocks have been machined to form 6-in. x 6-in. right circular cylinders and have been instrumented internally with a thermocouple array. One objective of early experiments with these instrumented coal blocks has been to determine bulk heat transfer properties during pyrolysis. The effects of an adherent ash and of the nonisotropic nature of the material have also been examined.

The first test of the modified block pyrolyzer was concluded March 20, using one of the instrumented blocks of western subbituminous coal. Thermocouples were positioned as shown in Fig. 4-4 to test the nonisotropic nature of the material and to determine the effect of the thermocouples themselves upon the temperature profiles observed. Results shown in Fig. 4-5 indicate that thermocouples positioned along a single radius

PHOTO 0189-75

Fig. 4-1. Large-block pyrolysis reactor system.

ORNL DWG. 75-798R1

Fig. 4-2. Heating rate of block pyrolyzer reactor (experiment No. 1, January 1975).

Fig. 4-3. Gas production rates during pyrolysis of an Appalachian bituminous coal.

SECTION A-A

Fig. 4-4. Instrumentation details for large-block pyrolysis coal sample.

ORNL-DWG 75-1054

EXPERIMENT NUMBER: 2
EXPERIMENT TIME: 7.5 HRS
REACTOR WALL: 725°C

Fig. 4-5. Thermal profiles produced by uniradial and staggered thermocouple arrays.

tend to produce higher temperature readings than thermocouples in staggered arrays. This is not unexpected and probably results because the metal thermocouples have a much higher thermal conductivity than coal. A future test is planned with spiral placement of the temperature probes which should eliminate this effect completely.

Although no specific cleavage planes were discernable in the test block, Figs. 4-5 and 4-6 are suggestive of nonisotropic thermal conductivity effects. Further tests will be required to substantiate this observation, and the superimposed effects of thermocouple placement and proximity to one another must be eliminated. This latter problem is particularly evident in Fig. 4-6, where the measured axial temperature profiles obviously show effects of heat transport along the thermocouples rather than through the coal block.

Analysis of gas-phase effluents produced by this experiment are not yet complete, but they will be included in the next monthly report. Ash residues have also been submitted to the Analytical Chemistry Division for determination of component minerals. It is interesting to note that when the char resulting from pyrolysis was cooled and subsequently exposed to the atmosphere, it was oxidized immediately and rapidly. Since the extremely pyrophoric nature of the char was unexpected, the rate at which air was supplied to the reactor was restricted, but not measured accurately. Figure 4-7 shows the temperature of the reacting char, observed as a function of time. Later experiments will utilize air injection to test this phenomenon more fully.

Three Experimental Engineering Section staff members visited with the in-situ gasification process research group at Lawrence Livermore Laboratories on January 14. Discussions centered upon the scope of studies being performed at LLL and upon those areas in which the ORNL Coal Program for in-situ process development could provide most needed support. A definite spirit of cooperation was generated at this first meeting which will be "followed up" by frequent interaction as experimental or program-related information becomes available.

Concurrent with the LLL visit, other ORNL staff members inspected the UCC Technical Center, South Charleston, West Virginia, to obtain information regarding the control and safe handling of carcinogenic coal-derived liquids. The most significant result of the trip was a greatly increased sense of awareness and concern on the part of all experimentalists in the program for the health hazard posed by these materials. The extent of this hazard has been evaluated and a formalized description of both the underlying safety philosophy and the operational procedures governing the conduct of experimental work in the Chemical Technology Division has been prepared. The document is being issued as a Laboratory Technical Manual. Comprehensive area and personnel monitoring programs are being implemented in cooperation with the Laboratory's Health Division.

ORNL-DWG 75-1055

Fig. 4-6. Observed axial and radial temperature profiles during block pyrolysis experiment.

ORNL-DWG 75-1056

EXPERIMENT NUMBER: 2

AIR FEED RATE: UNKNOWN

INITIAL CHAR TEMPERATURE: 25°C

Fig. 4-7. Oxidation of residual char after pyrolysis.

5. CHEMICAL RESEARCH AND DEVELOPMENT

G. P. Smith

Activities are reported here on mechanistic aspects of catalytic reduction by cobalt molybdate, catalytic methanation by molten salt systems, application of quantitative image analysis to coal petrography, and a preliminary study of coal constituents with a scattering electron microscope.

5.1 The Removal of Heteroatoms from Coal

R. A. Strehlow and L. L. Johnston

During the previous period a pulsed microreactor was designed and built. The reactor has been operated and applied to initial studies of the hydrogenolysis of thiophene and several thiophene derivatives and is designed to operate at gauge pressures of up to several atmospheres, with mixtures of $\text{H}_2\text{S}-\text{H}_2$ and with deuterium.

We have drawn tentative conclusions from the results so far. With regard to reduction in the presence of deuterium, other workers are reported to have observed no deuterium sulfide as a product, with only hydrogen sulfide being found. We have found that several cubic centimeters (STP) of exchangeable hydrogen is present on our 150-mg catalyst material and additional exchangeable hydrogen is found in the tabulation of the apparatus. As a consequence, the nonappearance of the expected deuterium sulfide may well be an artifact.

Our results have shown butene and butane as products of the reduction of thiophene with both temperature and contact time dependences. This agrees with earlier literature. The reaction of the butene (probable intermediate) with hydrogen to form butane appears to be inhibited by H_2S , but the reaction of thiophene does not.

An interesting finding during the period is not only that a mixture of $\text{H}_2\text{S}-\text{H}_2$ can be used to convert the catalyst to sulfide form, but that measurement of $\text{H}_2\text{S}-\text{H}_2$ ratio after a conversion appears to have a constancy characteristic of equilibrium relations. It appeared that over the range of 10^{-7} to 10^{-2} parts H_2S to H_2 the ratio of H_2S to H_2 could be easily used as a parameter related to the chemical condition of the surface. This parameter, which had been expected to be important, has been found to be significant to a moderate extent for ratios from 10^{-4} to 10^{-2} , but to a much greater extent at lower concentrations of H_2S . Since even a few hundred micrograms of thiophene were capable of generating a relatively long-lasting hydrogen sulfide concentration greater than a hundred parts per million ($\text{PH}_2\text{S}/\text{PH}_2 > 10^{-4}$), we have been studying the low concentration range using 1,3-butadiene, cis-2-butene, and ethylene

as models. The usefulness of these substances lies in the fact that a probable reaction scheme for thiophene reduction is

where

A = thiophene

B = butadiene

C = butene (with primes designating the isomers)

D = butane

Subscript, s, refers to surface species on the catalyst.

We have found that, at H_2S concentrations of 5-50 ppm, butene is reduced with high catalytic effectiveness to butane and, at higher levels of H_2S (>100 ppm), with considerably lower effectiveness. The reaction temperature used so far is $425 \pm 3^\circ C$ and the hydrogen pressure has usually been 2 atm.

We found that as little as 200 μg of water or 3 cc (NTP) of air injected into the reactor with its 150 mg of cobalt molybdate catalyst will markedly decrease the catalytic effectiveness for butane formation from 2-butene. This observation is consistent with the behavior we observed for butadiene under the same conditions, which will produce butene but not butane on the deactivated catalyst. Ethylene is not reduced under any experimental conditions used so far. This behavior, when fully interpreted, is expected to assist in understanding the hydrogenolysis reactions we plan to conduct on model compounds of higher molecular weight. Future work will also include studies in the presence of both hydrogen sulfide and water as well as comparisons of other catalytic materials.

5.2 Molten Salt Catalysis

M. H. Lietzke, A. S. Dworkin, and G. P. Smith

Design of a supported melt catalytic reactor was completed, components were ordered, and construction began toward the end of the quarter. A research laboratory was procured and outfitted. Catalytic tests using miniautoclaves began during the last month in the quarter. A number of melt systems were found to be active with respect to the methanation reaction. Some of these contained dispersed solid phases formed in situ. In general, most of the systems studied were too active to be usefully tested by the miniautoclave system and for that reason work with miniautoclaves was stopped so that the construction and testing of the dynamic reactor system could be expedited.

A general computer program was written to determine equilibrium product distributions and thermodynamic functions for an arbitrary number of simultaneous chemical equilibria. Production runs with this program were made for the simultaneous reactions

The results differed in several important respects from those previously reported (using computational schemes that were not described). We are checking the method and the results for possible errors.

5.3 Physical Structure of Coal

L. A. Harris and C. S. Yust

The study testing the applicability of quantitative image analysis to coal petrography has been progressing very satisfactorily. A publication presenting the results of an initial study on pyrite analyses has been completed. In brief, we have demonstrated that the percentages of pyrite (FeS) computed from the image analysis data are in excellent agreement with chemical analyses values. Additional studies covering such areas as size distribution of pyrite, total coal analyses, and conversion of optical intensity values from the image analysis instrument to reflectance data are in various stages of progress.

The transmission electron microscopy studies on high volatile bituminous coals are continuing. In all, four separate samples have been viewed and micrographs of structures considered significant have been obtained. The effort has been directed toward development of a method for thinning appropriate coal samples in order to carry out the

correlation of the optically identifiable constituents with the features observed by electron microscopy.

A cursory examination has also been carried out on the scattering electron microscope. Of particular interest has been the sulfur and iron determination in the coal matrix constituents surrounding pyrite fragments that appear to have developed in situ. Though these studies have been crude, initial indications are that the vitrinite surrounding a pyrite particle contained sulfur but not iron. This program will be pursued in order to better understand the relationship between inorganic and organic sulfur.

6. ANALYTICAL CHEMISTRY

W. D. Shults

Work reported here is carried out within the Analytical Chemistry and Chemical Technology Divisions and is sponsored by ERDA and NSF/RANN. The latter activities are part of the Ecology and Analysis of Trace Contaminants program for which William Fulkerson is the Principal Investigator.

6.1 Molecular Composition of Coal Conversion Process Streams (ERDA)

J. E. Mrochek and S. Katz

Preparative Separations of Coal-Derived Liquids

A modified Bureau of Mines--American Petroleum Institute procedure for the fractionation of heavy ends of petroleum has been used to separate four coal-derived liquids -- a medium oil from the COED process, a heavy oil from the Synthoil process, and two medium oils from the H-Coal process. The preparative separation is performed by eluting a dual silica-alumina column (200 cm x 1.9 cm, top half filled with fully activated silica, bottom half with fully activated alumina) with a series of solvents with increasing polarity. The sample is separated into saturate, monoaromatic, di-plus-triaromatic, and polyaromatic plus polar fractions corresponding to the changes in solvents.

The results for the four coal-derived oils (Table 6-1) show that the largest fraction from the COED process was the monoaromatic-containing fraction, and for Synthoil it was the polyaromatic plus polar fraction. The two products from the H-Coal process differed in the feed material -- one using Western subbituminous coal and the other Eastern bituminous coal. The largest fraction for the former was the saturate-containing fraction while for the latter it was the polyaromatic plus polar fraction.

Liquid Chromatographic Studies

A series of solid adsorbents have been evaluated for their ability to separate a COED medium oil. The adsorbents included: (1) erbium oxide (200-325 mesh), (2) basic alumina (200-325 mesh), and (3) particulate silica (20- and 7- μ m sizes). We had previously found that a gradient of solvent polarity -- even a gentle gradient -- caused the generation of chromatographic artifacts which interfered with the photometric detection of real chromatographic peaks. In order to elute compounds with a wide range in polarity, we attempted to use crude manual programming of column temperature at rates of from 10 to 20°C/hr. Isooctane was chosen as the moving phase because its wide liquid range (-100 to +116°C) was useful for temperature programming studies and it is relatively nonpolar.

Table 6-1. Preparative separation of several different coal-derived liquid products by liquid chromatography^a

Fraction	COED		Synthoil		H-Coal ^b		H-Coal ^c	
	g	%	g	%	g	%	g	%
Saturates	0.710	17.8	0.170	4.3	1.821	45.5	0.127	4.2
Monoaromatics	1.310	32.8	0.256	6.4	0.737	18.4	0.495	12.4
Di- and triaromatics	0.447	11.8	0.542	13.6	0.513	12.8	0.630	15.8
Polyaromatic plus polar-1	0.775	19.4	2.323	58.1	0.908	22.7	1.537	38.5
Polyaromatic plus polar-2	0.169	4.2	0.140	3.5	0.164	4.1	0.149	3.7
Additional			0.600	15.0				
Total recovery		86.0		99.9		103.4		74.6

^aFour grams of product loaded on a 200- x 1.9-cm column packed with fully activated silica (28 to 200 mesh) and fully activated alumina (80 to 200 mesh).

^bFrom Western subbituminous coal.

^cFrom Eastern bituminous coal.

Erbium Oxide as the Substrate. - Using a 150-cm column, a minimum temperature of near -70°C was required to separate out the early-eluting peaks, and chromatographic peaks continued to elute up to 140°C . About 30 distinct and reasonably reproducible (considering the manual temperature programming) peaks were separated.

Alumina as the Substrate. - Both 150- and 500-cm columns were tested. Retention of early-eluting compounds on this substrate was better than on erbium oxide. A minimum temperature of only -40°C was required to separate out early-eluting chromatographic peaks; peaks continued to elute up to about 110°C , which was the highest temperature possible because of gas being evolved from the column. The gas evolution problem continued, even with repetitive runs on the same column. Again, about 30 peaks were reproducibly obtained with better separation on the 500-cm column at a cost of twice the operating time (14 vs 7 hr).

Silica as the Substrate. - A 70-cm-long column (shorter because of the greater pressure drop) was tested. Retention of early-eluting compounds was improved compared to the other substrate tested, and only -10°C was required for this separation. Chromatographic peaks continued to be eluted at temperatures up to 140°C , with about 30 peaks separated.

In a general way, the pattern of eluted peaks was similar for the three substrates evaluated, suggesting that the mechanism of retention was general in nature. These separations are the best so far attained and appear to have some utility for preparative separations; however, much closer control of temperature will be necessary before we can achieve a reproducible elution pattern for "fingerprinting" these complex coal-derived liquids. The sample memory developing on these columns with their continuing use is somewhat disturbing since these adsorbents are relatively expensive.

Adsorbent Deactivation with Isopropanol. - Another method which is useful in effecting the elution of compounds having a wide range of polarities from an adsorbent system is the use of controlled chemical deactivation. Generally a reagent which is strongly adsorbed is introduced into the eluent and, depending upon the amount present, deactivates the more readily accessible adsorption sites. The problem is to maintain a reproducible degree of deactivation since continuing introduction of the species which is strongly adsorbed will eventually result in deactivating all sites and a pulsing of the deactivating chemical requires starting with a fully activated adsorbent each time.

We partially deactivated silica ($7\text{ }\mu\text{m}$ particle size) by introducing 0.1 and 0.01% isopropanol continuously in the isooctane eluent. The higher concentration deactivated the column too rapidly to be of any use. Deactivation with 0.01% isopropanol in isooctane proceeded slowly enough for studies of the elution of standards and samples of the COED medium oil. Peak shape for standard compounds was good and separation of a series of five polycyclic aromatic compounds was achieved. However, the problem of a buildup of column memory was again observed when

samples of the coal-derived liquid were chromatographed. Reproducible deactivation of the column was not achieved and elution positions for the standards varied because of this.

Analysis of a Mixture of Tar and Water

Analyses of material recovered from the tar trap of a quartz tube combustion experiment at Lawrence Livermore Laboratory have been completed. A total of 835.4 g of material was collected in the trap, with 85% or 713 g being an aqueous mixture containing 1.4% carbon. A total of 60 g (7.2% of total) of a tarry solid (50% C, 0.39% S, 0.33% ash) with a heating value of 9900 Btu/lb was recovered. The final fraction was a pentane-soluble oil which, after air-drying, weighed 71.6 g (8.6% of total); it contained phenol, cresols, methylated anisoles, and a number of saturated hydrocarbons (C₂₁ to C₂₇) as major constituents. The material contained 0.58% sulfur and had a heating value of 17,700 Btu/lb. Material balance (by weight) for the contents of the trap was 101% of theoretical, which was reasonable considering the nature of the trapped material.

Improved Sensitivity for the ORNL Fluorescence Flow Monitor

The sensitivity of the fluorescence flow monitor has been markedly improved and its usefulness extended to additional compounds of interest. The improvement in sensitivity is due to evaluation of the relative stability of various power supply and control settings so as to optimize the signal with minimum noise. The extension to additional compounds is by use of a broader emission filter. These improvements appear to make the fluorescence detector superior to the uv absorption monitor for chromatography of coal-derived liquids.

6.2 Gas Chromatographic Studies (NSF/RANN)

M. R. Guerin, A. D. Horton, C.-h. Ho, and I. B. Rubin

Research on coal-derived product oils and gases has been centered on health and environmental problems associated with handling of the products by operating personnel, and with the effect of the storage, use, and waste disposal of the products on the general environment.

Product oils, in general, have been shown to have significantly more of the carcinogenic polyaromatic hydrocarbons (PAH) than equivalent amounts of tobacco condensate. The PAH content of the product oils tested have up to 100 times as much benz(a)pyrene as that found in tobacco condensate, and a larger proportion of the 4- and 5-membered rings in general, plus 7-membered rings not found in tobacco products. Many of the PAH's have been identified by co-chromatography. A solvent extraction scheme has been developed for application to product oils. Semicontinuous, multistage extractions are carried out by continuous stirring of solutions in separatory funnels, with constant addition of

solvent, and overflow to a second separatory funnel, where the second stage extraction takes place, and continuing in this manner until all fractions are separated. The fractions are evaporated by a rotary vacuum evaporator, the residue is weighed to obtain a material balance, and the residue is redissolved in a suitable solvent for further analyses. All of the fractions have been tested for mutagenicity. Gas chromatographic component profiles of each fraction, and of the trimethylsilyl derivatives of each fraction have been obtained, as have the gas chromatographic sulfur component profiles. These profiles are preliminary to the development of methodology for the determination of specific components in the fractions, to the biological testing of the fractions (blind assay), and to the application of reaction techniques for the class elucidation of the components in the fractions. Sulfur compounds which affect catalysts used in producing the oils and gases, and which may have biological significance, have been investigated with respect to classification, and later, identification of these compounds. Attempts to use mercuric salts to form complexes with sulfur compounds were successful for components found in gaseous products. Mercuric salts are not applicable to sulfur components in the middle-and-high boiling range. Copper-form ion exchange resins have been successful in separating the middle-and-high boiling range compounds from other hydrocarbons. Partial success in separating certain sulfur compounds in the middle boiling range was accomplished by liquid chromatography of the oil on a large Florisil column using hexane as a solvent. Sulfur component gas chromatographic profiles were obtained for each 100-ml fraction, sulfur-rich fractions were combined, the solvent was removed by evaporation, and the concentrate was rechromatographed on a small Florisil column. An enriched sample suitable for mass spectrometric analysis of about 15 sulfur compounds was obtained in this manner.

6.3 Routine Analytical Operations

W. R. Laing

Preparation of Laboratory for Routine Coal Analysis

During this period room E-259 in building 4500S has been cleaned out and prepared for use as a coal analysis laboratory. Heavy duty equipment racks, furnaces, and utility lines, formerly used by the Reactor Chemistry Division, were removed. Laboratory benches and service and utility lines, which were necessary for use in an analytical chemistry laboratory, have now been installed, and the laboratory is ready for use by the Analytical Chemistry personnel.

Analysis of Samples Related to Coal Programs

Ultimate and proximate analysis of coal and char samples have been made on a routine basis. In addition carbon, hydrogen, nitrogen, and sulfur determinations have been made on coal-derived oil samples. Two sets of gas samples derived from pyrolysis tests have been analyzed for N, CO, and CH₄.

A Leco high frequency combustion titration procedure is being adapted for the determination of sulfur in samples where the amount of sample is limited.

A furnace, and platinum crucibles, for use in testing oils and coals for volatile matter, were procured and are now in use for routine tests.

L. J. Brady and H. G. Davis visited the Pittsburgh Energy Research Center and the Bureau of Mines Coal Laboratory and observed the techniques and methods being used in these laboratories for the analysis of coal and coal-derived oils. Information acquired during these visits will be helpful in the future when we are asked to test similar samples.

7. SYSTEMS STUDIES OF COAL PRODUCTION (NSF-RANN)

R. S. Carlsmith, R. L. Spore,
E. A. Nephew, and W. W. Lin

The Systems Studies of Coal Production Program is designed to develop detailed engineering/economic models of coal production in the United States, and to apply those models: (1) to evaluate the prospects for increasing the nation's coal supply, and (2) to analyze the impact of policies which may affect the coal industry. The report summarizes progress in this program for the period January 1 to March 31, 1975. The report is divided into sections corresponding to the independent but related studies which comprised the program's activities.

7.1 The Costs of Coal Surface Mining and Reclamation in Appalachia

This study was designed to estimate the costs of obtaining alternative levels or qualities of reclamation under mining conditions typical of the Appalachian coal province. The study consists of engineering and cost analyses of 28 individual model mines chosen to represent various combinations of mining and reclamation techniques applied to three alternative slopes (15-deg, 20-deg, 25-deg) and two alternative overburden-to-coal ratios (maximum overburden heights of 60 and 90 ft). Progress in various portions of this study is described below.

Estimation of Total Costs (Required Receipts)

To be useful for policy analysis, the appropriate measure of the cost of mining and reclamation is total cost, which includes not only the variable or operating cost of unit operations (reported earlier¹), but also certain nonoperating expenditures (supervision, union welfare payments, royalties, etc.) as well as the cost of capital. The cost of capital includes both capital recovery (depletion and depreciation) and opportunity costs, or the rate of return that could have been achieved from an alternative investment. Thus, in this study, total cost is estimated as required receipts, or the minimum acceptable selling price which would generate an annual net cash flow [revenue - (operating costs + expenditures) - taxes] sufficient to pay off the investment principle over the life of the mine and to pay a specified return on the unamortized principle. The estimating procedure employed, commonly called discounted cash flow rate-of-return analysis, determines the required cash flow as that constant annual amount whose discounted present value over the life of the mine is equal to the discounted present value of investment at a specified after-tax rate of return. Cash flows and selling prices corresponding to three alternative rates of return (8%, 12%, 15%) are used in this study. As an example, Table 7-1 presents the total cost and investment analysis for Model Mine No. 1.

Table 7-1. Total cost and investment analysis,
Model Mine No. 1, 1974

(161,300 tons/year, 12% rate of return)

Item	\$/ton
A. Required receipts	7.99
B. Expenditures	
Operating cost	4.95
Supervision	0.16
Payroll overhead	0.35
Union welfare	0.60
Royalty	0.20
Taxes, ins. (except income tax)	<u>0.14</u>
Total expenditures	6.39
C. Net receipts before taxes (A-B)	1.60
D. Depreciation (straight-line)	0.78
E. Depletion, 0.5 (C-D)	0.41
F. Taxable income (C-D-E)	0.41
G. Corporate income tax	0.16
H. Net profit per ton (F-G)	0.25
I. After-tax cash return (C-G)	1.44
J. Investment, per ton of annual output	
Structures and equipment, 20 years	3.03
Structures and equipment, 10 years	0.73
Structures and equipment, 5 years	3.15
Working capital	<u>0.50</u>
Total initial investment	7.41

Revisions in Variable Cost Estimates

Previous estimates of the variable costs of production for each mine were based on equipment operating costs and labor wage rates prevailing in Appalachia in 1972. To enhance the usefulness of the study's results, given the recent high rates of inflation, it was necessary to update the cost estimates prior to final publication.

The revisions in cost were prepared by applying cost indices² to each of the components of equipment operating costs (fuel, lubricants, tires, and repair parts), as well as to wage rates and materials costs. Table 7-2 indicates the magnitude of the impact of inflation by comparing the estimates of variable cost for 1972 and 1974 for Model Mine No. 1.

During the process of making this revision, other modifications to the analysis method also were made, primarily by increasing the amount of computer processing. These modifications will enhance the flexibility and usefulness of the model mine analyses by minimizing the effort required to perform additional subsequent revisions to reflect (1) future possible cost escalations, or (2) changes in the specific reclamation provisions to be evaluated (such as those contained in the recent federal surface mining bill).

7.2 Process Analysis Estimation of Cost Functions for Coal Mining in the United States

This study consists of the development of detailed engineering/economic models of coal production capable of analyzing and predicting the impact of alternative energy and environmental policies on the cost and supply of coal. The analytical technique employed - linear programming process analysis - simulates mine operators' decisions regarding how to produce a given level of output as the choice among alternative production methods or processes, subject to constraints on input availabilities. The cost-output relationship then is derived as the set of cost estimates corresponding to those combinations of processes sufficient to produce alternative levels of output at least cost.

The first application of the process analysis model was an analysis of the short-run impact of surface mining regulations on the cost and supply of coal from three subregions of Appalachia.¹ Recent activities have been devoted to the validation of the results of this study and are reported on below. Additional aspects of the study include the development of long-term dynamic models of coal production and investment. Progress in this portion of our work also is reviewed below.

Table 7-2. Changes in variable cost of unit operations,
1972-1974 (Model Mine No. 1)

Unit operation	Cost/ton	
	1972	1974
1. Access road construction	0.04	0.05
2. Clearing and scalping	0.01	0.01
3. Topsoil removal and replacement	0.06	0.10
4. Drilling and shooting	0.99	1.77
5. Overburden removal	1.29	2.13
6. Coal loading and hauling	0.23	0.34
7. Backfilling and grading	0.14	0.22
8. Revegetation	0.05	0.05
9. Auxiliary	<u>0.14</u>	<u>0.27</u>
Total variable cost	2.95	4.95

Table 7-3. Analysis of aggregation bias

Region or state	Total variable cost of 1972 output (\$)	Quantity supplied at price of \$4.50/ton (millions of tons/year)
1. Northern Appalachia	253,357,330	70.42
2. Individual states		
Pennsylvania	91,564,128	24.95
West Virginia	21,875,072	13.95
Maryland	4,441,794	2.40
Ohio	<u>138,196,480</u>	<u>25.70</u>
Total	256,007,474	67.00
Difference (1-2): total	-2,720,144	3.42
per ton	-0.04	

Validation of Previous Results

Ideally, a process model of coal production for a given regional portion of the industry would be written as a weighted average of process analysis models for each mine in that region. Unfortunately, the technology associated with each mine is not known, nor would it be feasible to obtain such data. Therefore, the concept of the representative or typical firm is used to describe the industry production function. However, employing this approach introduces the possibility of aggregation bias in the results since, by using an industry production function, one assumes that while productive inputs are physically separated they are readily transferable between mines. While such an assumption may not be too restrictive, since mining firms typically operate more than one pit or mine and do transfer inputs between them, an investigation of possible bias is warranted nevertheless.

One test for possible bias that has been performed was a comparison of the results of the aggregate model for the Northern Appalachian region with the sum of the results for models of the individual states within that region. Table 7-3 presents the results of that analysis. The results suggest that aggregation bias is minimal; i.e., the aggregate model appears to underestimate the costs of production by approximately 4¢ per ton while overestimating coal supply at a price of \$4.50 by less than 4 million tons.

Development of Long-term, Dynamic Model

One of the major components of the long-term dynamic model of coal production and investment now being developed is a sales forecasting model for each coal-producing region. The forecasting model is designed to simulate miners' decisions regarding how much to produce in given future time periods. The model is formulated as a single equation to be estimated from historical data. A tentative version which recently has been formulated is:

$$S_t = f(S_{t-1}, S_{t-2}, S_{t-3}, FPR_t, FPR_{t-1}, ACC_t, ACC_{t-1}),$$

where

S_t = coal production in year t

$S_{t-1}^*, S_{t-2}, S_{t-3}$ = coal production in years $t-1, t-2, t-3$

FPR_t = fuel price ratio in year t =

$$\frac{\text{composite wholesale price index} \\ \text{for oil and gas}}{\text{wholesale price index for coal}}$$

FPR_{t-1}^* = fuel price ratio in year t-1

ACC_t^* = aggregate coal consumption in year t

ACC_{t-1} = aggregate coal consumption in year t-1

Preliminary results from the application of this model for surface mining in Northern Appalachia show the starred variables to be significant, with an overall $R^2 = 0.91$.

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